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69/54, C12P 7/42, 7/62

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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHODS OF MANUFACTURING DERIVATIVES OF β -HYDROXYCARBOXYLIC ACIDS

(57) Abstract: Preparation of derivatives of β -hydroxycarboxylic acid, including β -hydroxycarboxylic acid esters, α,β -unsaturated carboxylic acids, esters of α,β -unsaturated carboxylic acid, and alkoxy derivatives. The β -HCA may be derived from a biomass fermentation broth.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/09095

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C57/05 C07C57/045 C07C67/08 C07C69/675 C07C51/377 C07C67/31 C07C69/708 C07C67/327 C07C69/54 C12P7/42 C12P7/62		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07C C12P		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, BEILSTEIN Data, CHEM ABS Data, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 211 846 A (LAFFERTY ROBERT M) 8 July 1980 (1980-07-08) example 13	1-8
X	----- P. A. LEVENE, H. L. HALLER: "THE CONFIGURATIONAL RELATIONSHIPS OF 2-HYDROXY, 3-HYDROXY AND 4-HYDROXY ACIDS" JOURNAL OF BIOLOGICAL CHEMISTRY., vol. 69, 1926, pages 165-173, XP008019487 AMERICAN SOCIETY OF BIOLOGICAL CHEMISTS, BALTIMORE, MD., US ISSN: 0021-9258 page 167 ----- -/--	1-7
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
11 July 2003		13. 11. 2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Kardinal, S.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EMIL FISCHER: "Zur Kenntnis der Waldenschen Umkehrung IV" CHEMISCHE BERICHTE., vol. 42, 1909, pages 1219-1228, XP001149222 VERLAG CHEMIE GMBH. WEINHEIM., DE ISSN: 0009-2940 page 1221, paragraph 3 -----	1-7
A	W. A. DRUSHEL, W. H. T. HOLDEN: "Über die Darstellung und Eigenschaften der Hydracrylsäureester" CHEMISCHES ZENTRALBLATT, vol. 87, 1916, pages 142-143, XP008019488 XX, XX page 142, paragraph 3 - page 143, paragraph 2 -----	1,8
A	J. HASEGAWA ET AL.: "Production of beta-Hydroxypropionic Acid from Propionic Acid" JOURNAL OF FERMENTATION TECHNOLOGY, vol. 60, no. 6, 1982, pages 591-594, XP008019541 TOKYO, JP page 594, left-hand column -----	1,8
A	W. RIEMENSCHNEIDER: "Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 1999 Electronic Release" 1999, WILEY-VCH, WEINHEIM, GERMANY, XP002247378 Esters, Organic - Production 5.1.1 Catalysts -----	1,8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/09095

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8 (complete)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8 (complete)

Preparation of a beta-hydroxycarboxylic acid ester from the corresponding acid or salt and an alcohol in the presence of a catalyst, in the absence of solvent other than the alcohol under anhydrous conditions at atmospheric pressure and a temperature less than the reflux temperature.

2. claims: 9-13 (complete)

Preparation of a beta-hydroxycarboxylic acid ester from the acid and a C1-C7 alcohol in the presence of a catalyst in a water-immiscible extractant.

3. claims: 14-42 and 49 (complete)

Preparation of an alpha-beta-unsaturated carboxylic acid or salt or ester thereof by dehydration of a beta-hydroxycarboxylic acid or salt or ester thereof.

4. claims: 43-48 (complete)

Preparation of an alkoxy derivative of a beta-hydroxycarboxylic acid by heating an aqueous solution comprising a beta-hydroxycarboxylic acid, an alcohol and a basic catalyst in a closed reactor.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/09095

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4211846	A	08-07-1980	CH 621148 A5 15-01-1981
			CH 620706 A5 15-12-1980
			AU 513017 B2 06-11-1980
			AU 2763677 A 08-02-1979
			BE 857486 A1 06-02-1978
			CA 1100896 A1 12-05-1981
			DE 2733202 A1 09-02-1978
			DK 347077 A 05-02-1978
			FR 2369343 A1 26-05-1978
			GB 1542028 A 14-03-1979
			IT 1116790 B 10-02-1986
			JP 53018794 A 21-02-1978
			NL 7708633 A 07-02-1978
			SE 7708845 A 05-02-1978
